Progressing Insensitive Munitions: Benefits and Techniques for Proactively Addressing Environmental Regulations

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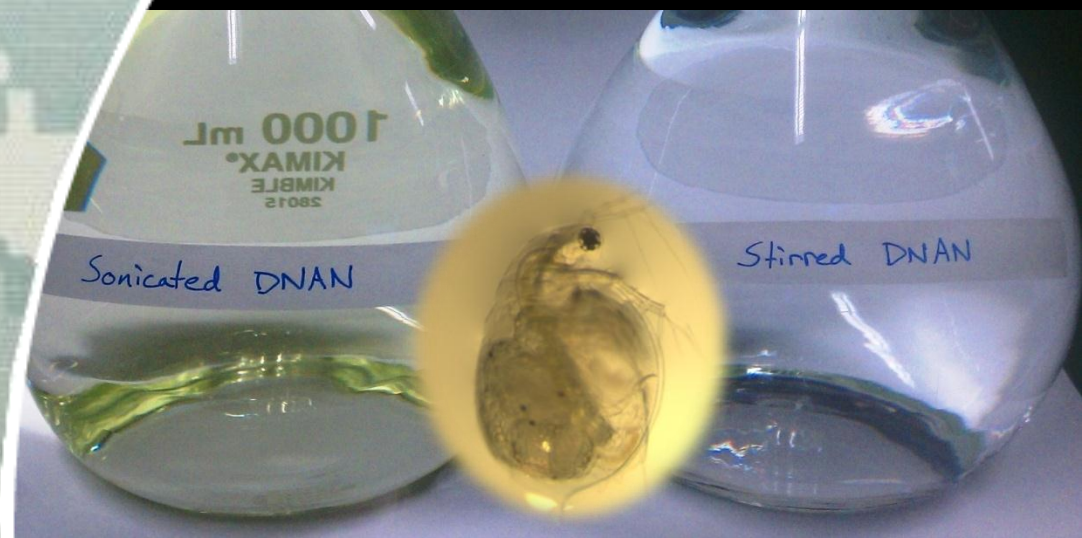

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Presentation Outline

- Insensitive munitions
- Environmental regulations
- ERDC overview
  - Testing Capability
  - DNAN toxicity (if in environmental media)
  - Insensitive munition research
    - Where will it go?
    - What form will it be in?
    - What is the environmental liability?

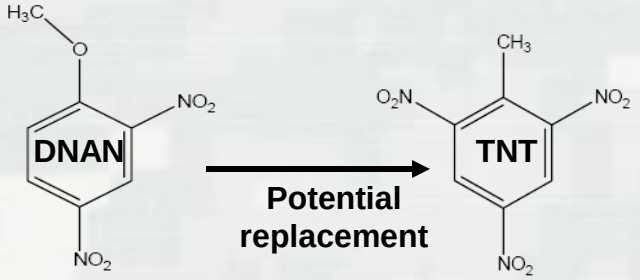
Insensitive Munitions

- US Military initiative: replace traditional munitions compounds (MCs) with insensitive munitions (IMs)
- IMs: less susceptible to inadvertent detonation due to accidental stimulus
- *Little is known about the toxicity of IMs / DNAN in ecological receptors.*

Insensitive Munitions can Protect Soldiers. Will they also have lower relative impact on the Environment?

IM	Ingredients	Application
IMX-101	**DNAN**, NTO, NQ	Artillery projectile
IMX-104	**DNAN**, NTO, RDX	Mortar systems
PAX-48	**DNAN**, NTO, HMX	Tank ammunitions
PAX-21,41	**DNAN** melt case	Fielded mortar

2,4-dinitroanisole



Solubility: 191 – 276 mg/L (≈25 °C)
Boddu *et al* 2008. *J Chem Eng Data* 53: 1120-5

- History
  - Previously used due to TNT scarcity
  - 10% energetic impact; one less nitrate group
- Unknown toxicity
  - Overly conservative safety factors
    - Acute-to-chronic ratios: 0.01
    - Most ACRs range from 0.10 – 0.15
- Treatment
  - Waste water treatment
  - Aesthetic concerns (yellow water)
    - 2,4-dinitrophenol, 130 ppb in waste water
    - Electrochemistry and Fenton's Reaction (David Gent, ERDC)
- Consideration of
  - Impacts of treatment
  - Parent vs. degradation compounds toxicity
  - Stability

Treatment options for IMX & RDX Production wastewater

- Determination of Available Treatment Options
  - Advanced Oxidation Process (DNAN & NTO)
  - Reductive (RDX &TNT)
  - Biological (Anaerobic/Aerobic)
- Characterization of Waste Stream
- Bench Studies of Promising Approaches
- Full-Scale Pilot Treatment Systems


RDX Waste stream Characterization


Photochemical Oxidation DNAN

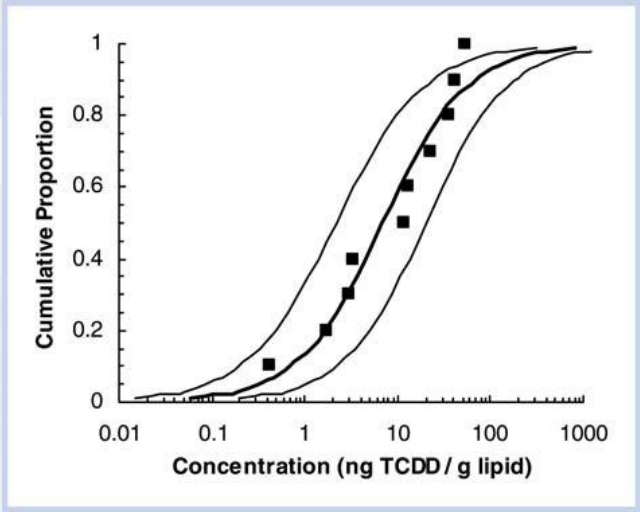

Electrochemical Reactor RDX Treatment

Environmental Regulations

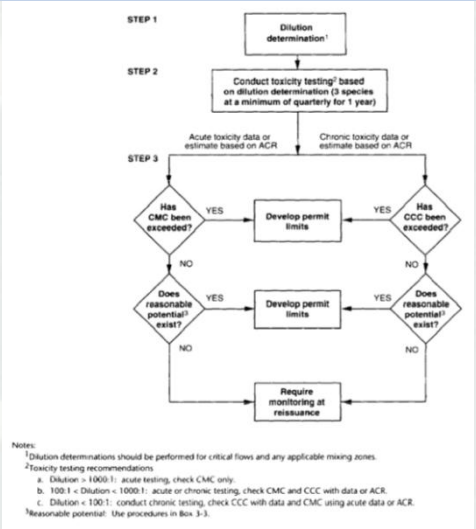
- Clean Water Act → protect waterways and impose / enforce regulations
  - Section 101 – discharge of pollutants at toxic levels is prohibited
  - Rules – new rules to be implemented by CWA
  - Code of Federal Regulations – existing regulations and rules
  - Total Maximum Daily Load (TMDL) – effluent cannot exceed
    - Amount of specific pollutant that can be discharged without violating WQS
    - Account for temperature, seasonal flow rates
  - Whole Effluent Testing (WET) - 40 CFR Part 122.44(d)
    - Aggregate toxic effect to aquatic organisms from all pollutants contained in a facility's wastewater (effluent).

Derivation of WQC

- Invertebrate, vertebrate and plant bioassays
  - Acute WQC – 8 species
  - Chronic WQC – 3 species
- Protective of 95% of species (species sensitivity distribution

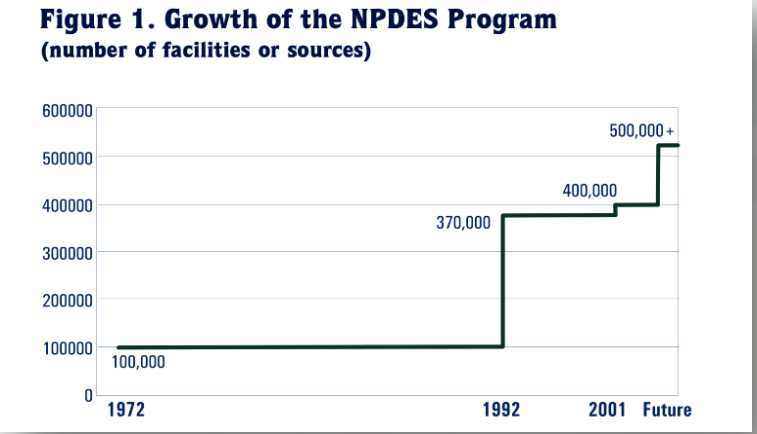


Steevens et al. 2005. Integr Environ Assess Manag 1(2): 142–151



NPDES permitting

- Required for “All facilities which discharge *pollutants* from any *point source* into waters of the United States”
  - Who needs it
    - Municipal waste water systems
    - Municipal / industrial storm water systems
    - Industries / commercial facilities
    - Animal feeding operations
  - Effluent Limits - TDML
    - Waste treatment
  - Mixing zone
    - State determines size
    - WQC, if available
    - “Should not cause lethality to passing organisms”
  - Worst case flow scenarios for effluent dilution
    - Lowest flow in 10 years (7Q10)
  - Monitoring, reporting, repeated testing



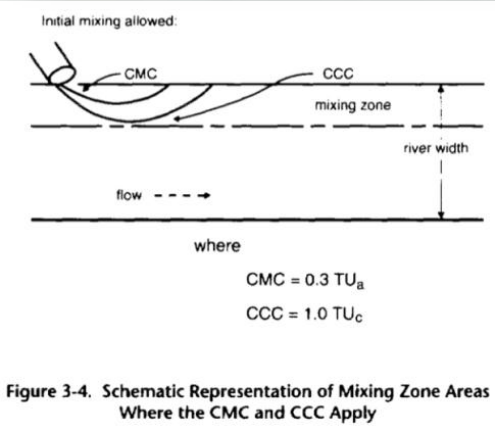
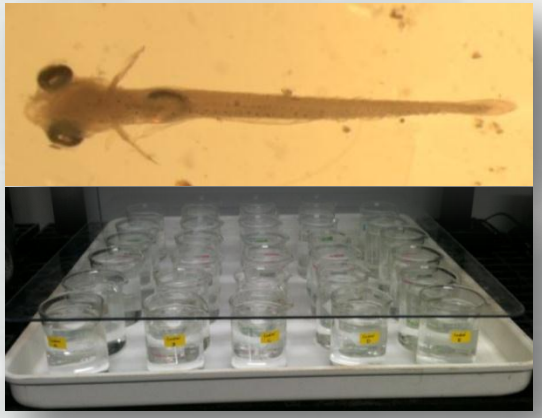


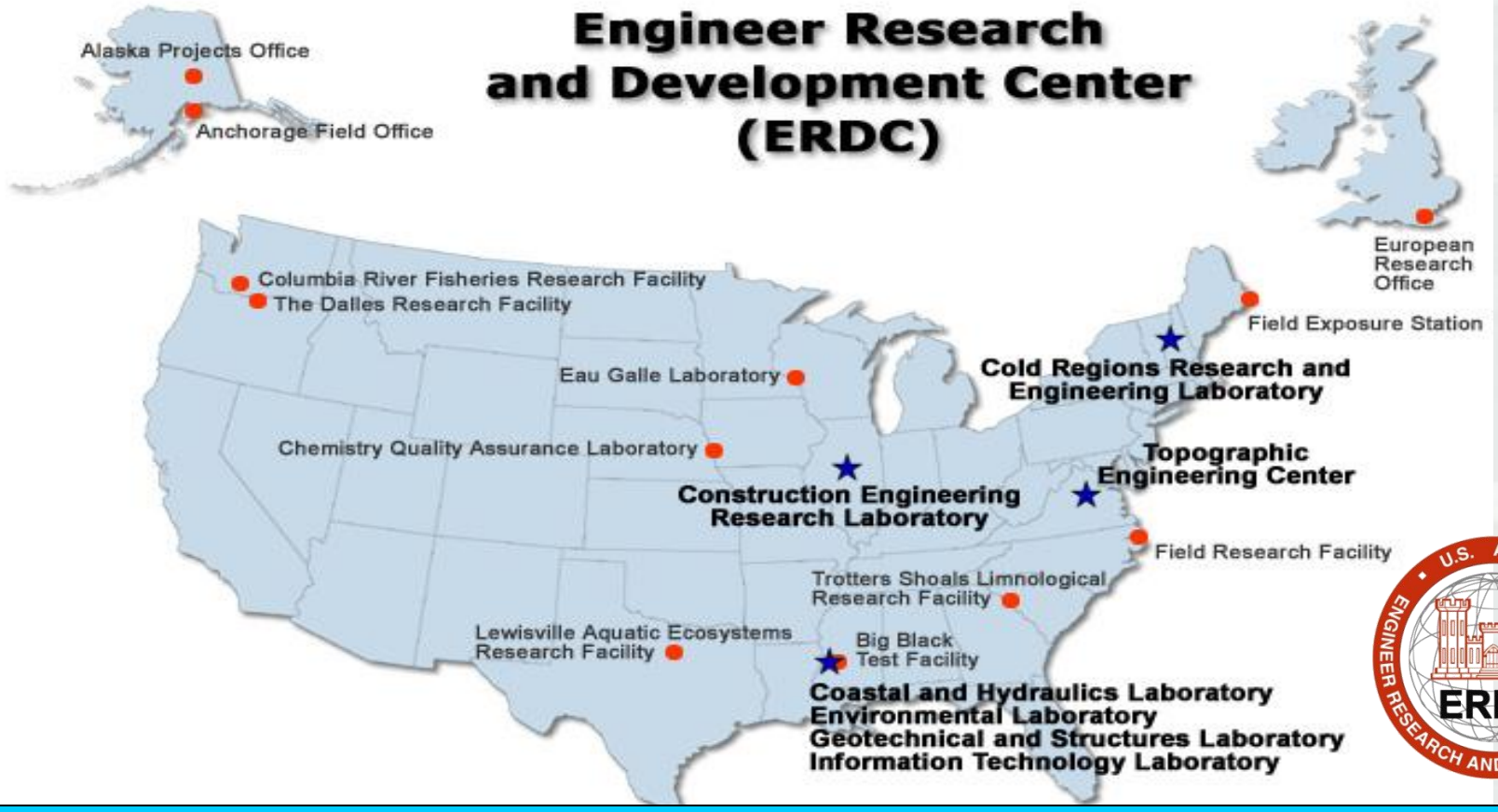
Figure 3-4. Schematic Representation of Mixing Zone Areas Where the CMC and CCC Apply

Benefits of bioassay testing

- Proactive knowledge of the toxicological effects of insensitive munitions
  - Establish WQC
  - Account for degradation / unknown synergies in complex effluent mixtures
- Reduce cost incurred by
  - Short-term: Allow manufacture and associated discharges to continue
  - Long-term: avoid future litigation, clean-up costs by employing necessary environmental controls
- Comparatively, paying for bioassays is the cheaper option
  - Cost for acute bioassays $0.5 – 2K (plus analytical)
  - Cost for chronic bioassays $1 – 5K (plus analytical)
  - Cost for no action / indecision: ?????



Engineer Research and Development Center (ERDC)

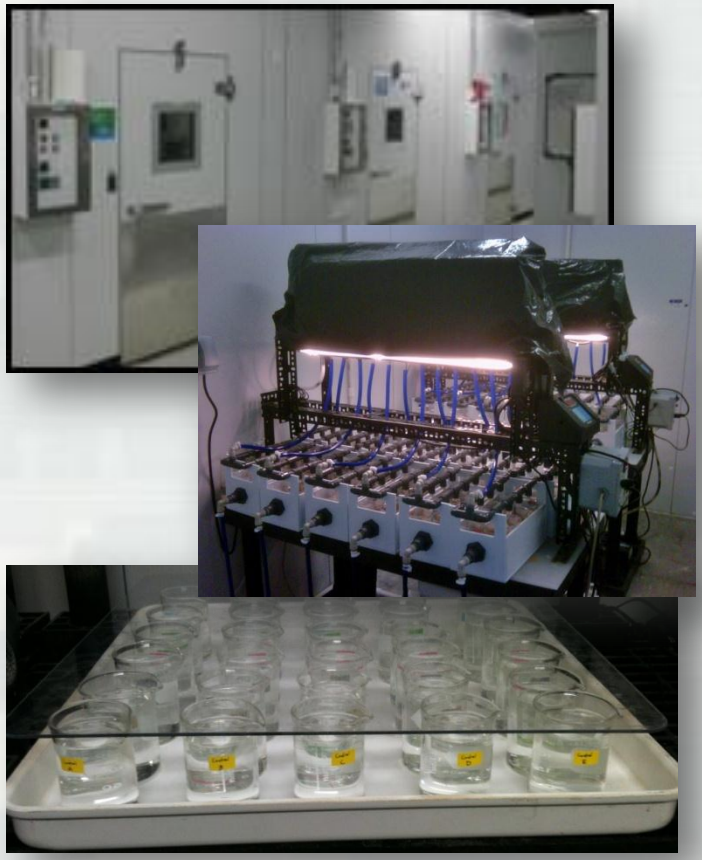


Five primary areas to support the Army and the Corps:

- Warfighter Support – geospatial information; system development; operational support; force protection; and force projection and sustainment
- Installations – transformation; operations; and environmental issues
- Environment – remediation and restoration; land planning, stewardship and management; threatened and endangered species; and cultural resources
- Water Resources – infrastructure, water resources, environmental issues, and navigation; and flood control and storm damage reduction
- Information Technology – informatics; geospatial technologies; computational services; high performance computing applications

ERDC
Environmental Toxicology Center

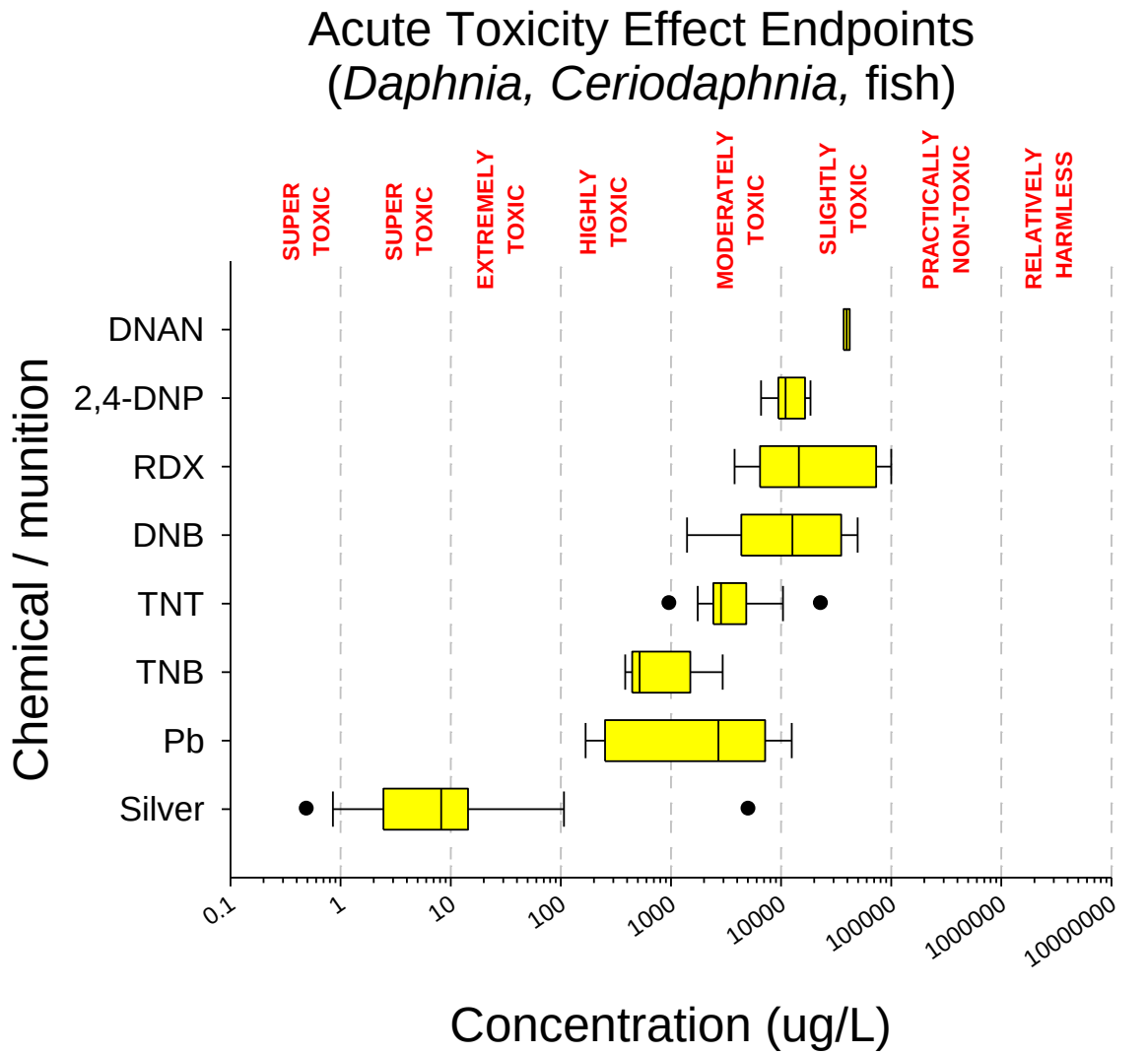
- High quality ecotoxicological data generation
- Advance Army's mission while achieving environmental compliance
- Consideration of geochemistry and bioavailability



Types of bioassays

Medium	Common Name	Organism	Acute toxicity	Chronic toxicity	Bioaccum-ulation
Freshwater	Water flea	*Daphnia magna/pulex*	X	X	
	Water flea	*Ceriodaphnia dubia*	X	X	
	Fathead minnow	*Pimephales promelas*	X	X	
	Zebra fish	*Danio rerio*	X	X	X
	Green algae	*Pseudokirchneriella*		X	
	Northern Leopard Frog	*Rana pipiens* tadpoles	X	X	X
Freshwater sediment	Amphipod	*Hyalella azteca*	X	X	X
	Midge fly	*Chironomus tentans/dilutus*	X	X	
	Worm	*Tubifex tubifex*	X	X	X
	Black worm	*Lumbriculus*			X
	Asiatic clam	*Corbicula fluminea*			X
Estuarine/marine water column	Mysid shrimp	*Americamysis bahia*	X		
	Sheepshead minnow	*Cyprinodon variegatus*	X	X	
	Silverside	*Menidia beryllina*	X		
Estuarine/marine sediment	Amphipod	*Leptocheirus*	X	X	X
	Amphipod	*Ampelisca abdita*	X		
	Amphipod	*Eohaustorius estuarius*	X		X
	Polychaete worm	*Neanthes*	X	X	X
	Bent nose clam	*Macoma nasuta*			X
	Polychaete worm	*Nereis virens*			X
	Hardshell clam	*Mercenaria*			X
	Clam	*Yoldia limatula*			X
	Copepod	*Amphiascus tenuiremis*	X	X	
Soil	Earthworm	*Eisenia fetida*	X	X	X

Relative DNAN toxicity



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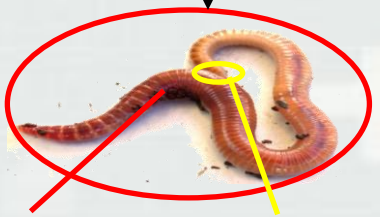
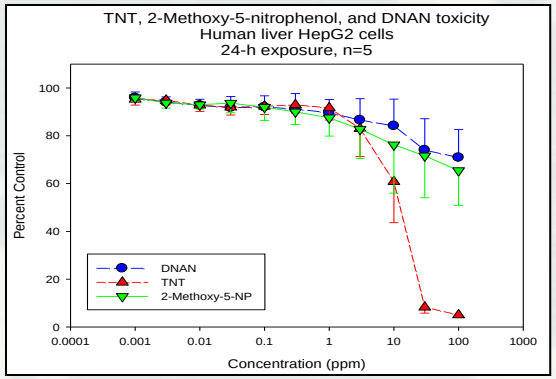
Talmage et al 1999; US EPA ECOTOX accessed 30 April 12; this project

Computational Chemistry and Toxicity of DNAN

- **Funding source**: ERDC Environmental Quality Basic Research Program 6.1 (TDs: Savoie, Ferguson)
- **Duration**: FY08-FY10
- **PIs**: Brasfield, Hill, Coleman
- **Objective**: Combine computational chemistry and exposure assessment tools to predict the terrestrial environmental fate and biological impacts of DNAN.
- **Results**: Data obtained through acute and sub-chronic terrestrial studies suggest that DNAN is **less toxic** than TNT. Computational predictions indicate the formation of stable, but more toxic, degradation product under alkaline hydrolysis.
- **Bottom Line Up Front (BLUF)**: DNAN resulted in lower toxicity to relative to TNT compounds in terrestrial exposures

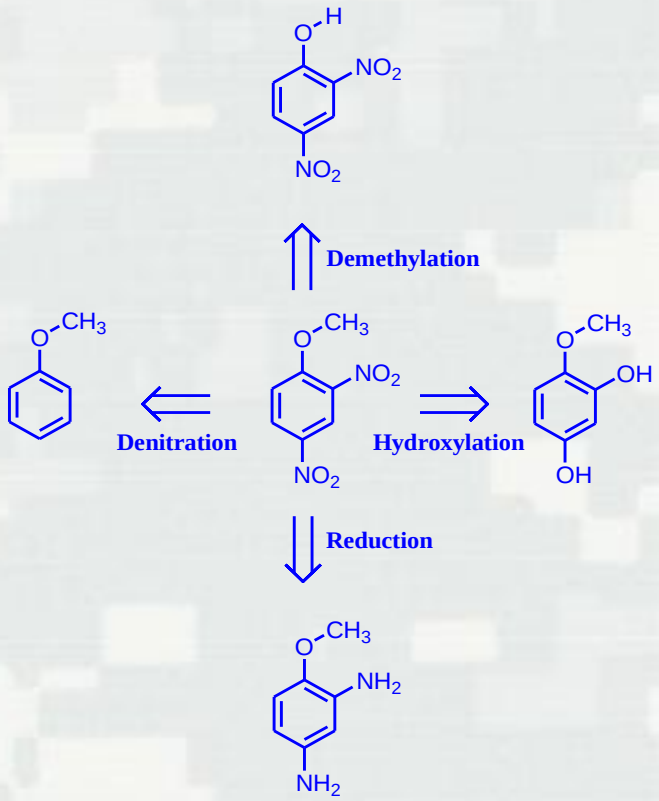


Dermal Exposure **Ingestion**



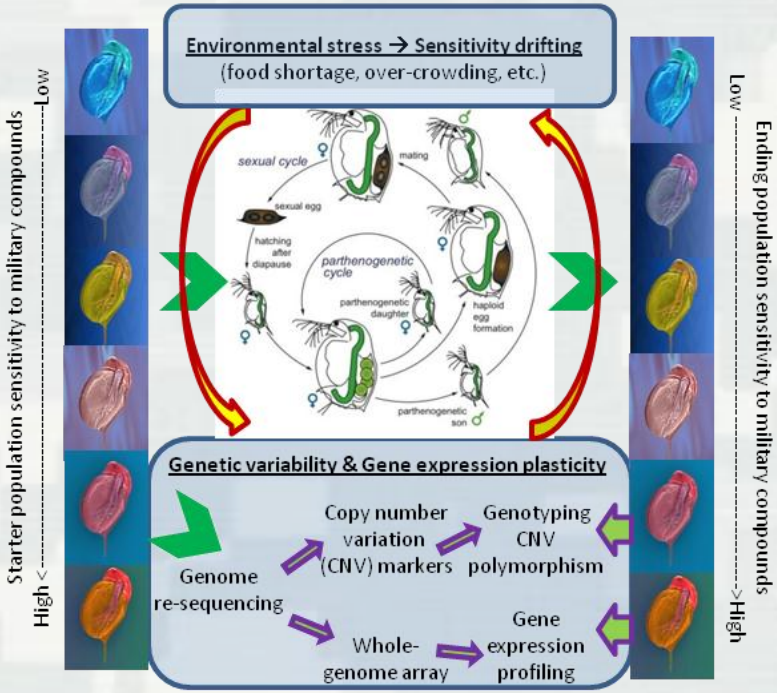
Bioavailability and Degradation Pathways for DNAN

- **Funding source**: ERDC Environmental Quality Basic Research Program 6.1 (TDs: Savoie, Ferguson)
- **Duration**: FY12-14
- **PIs**: Brasfield, Crocker, Lotufo, Mannion
- **Objective**:
  1. Determine potential for bioaccumulation and food-chain transfer of DNAN
  2. Characterize mechanisms and metabolites of biological degradation of DNAN
  3. Investigate the toxicity and bioaccumulation potential of the resulting DNAN metabolites.
- **Results**: bioaccumulation kinetics, microbial degradation pathways
- **BLUF**: It will break down, we need to know whether those compounds are a problem.



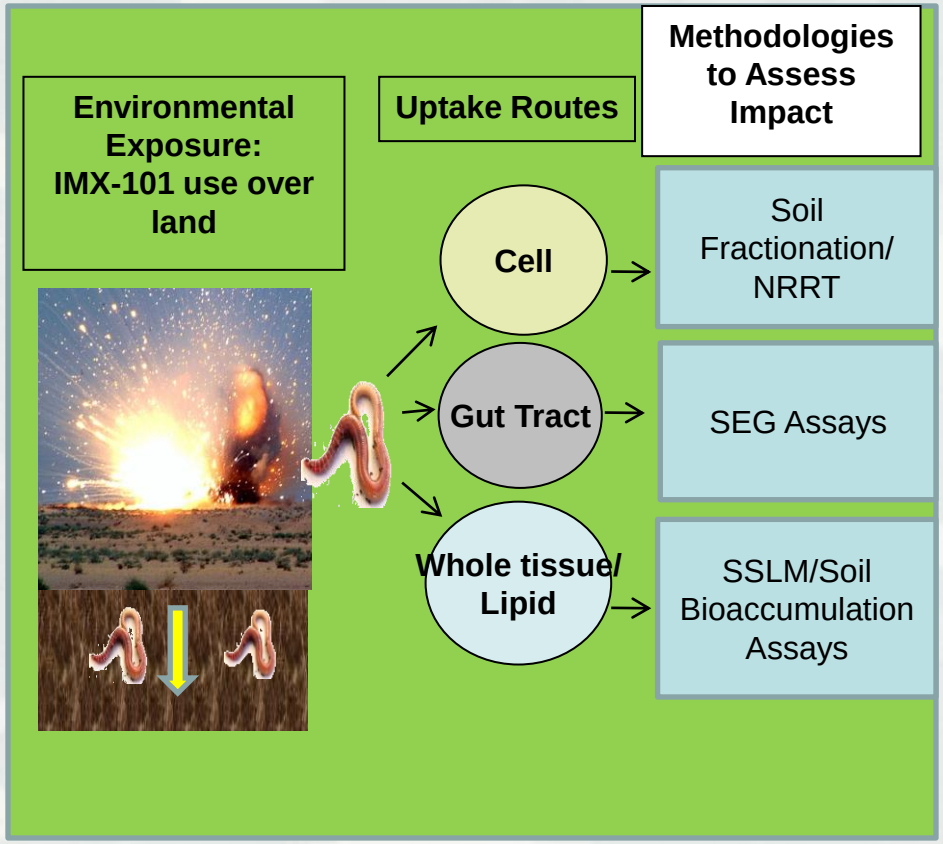
Population-level Temporal Drift in Sensitivity to Army Relevant Chemicals: Phenotypic Plasticity or Genetic Variation

- **Funding source**: ERDC Environmental Quality Basic Research Program 6.1
- **Duration**: FY12 - 14
- **PIs**: Kennedy, Gong, Laird, Lance
- **Objective**: Provide understanding of how accurately laboratory toxicity tests represent the chemical sensitivity of natural resident populations adjacent to DoD sites
- **Results**: aquatic toxicity related to genetics
- **BLUF**: Preliminary results suggest DNAN is less toxic than many traditional MCs and field and lab populations give slightly different toxicity reference values.



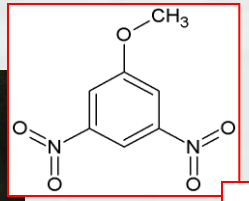
Assessing the Bioavailability of IMX-101 to Terrestrial Biota through Development of Innovative Toxicological Screening Methodologies

- **Funding source**: ERDC Environmental Quality Basic Research Program 6.1 (TDs: Savoie, Ferguson)
- **Duration**: FY12 - 14
- **PIs**: Coleman J., Johnson D., Seiter J., Bednar A.
- **Objective**: Determine bioavailability of IMX-101 in terrestrial invertebrates and systems through bench-scale and synthetic screening analysis
- **Results**: initial results show minimal degradation of IMX-101 with varied pH and light conditions
- **BLUF**: Bench-scale and synthetic screening bioassays will significantly reduce time and cost while increasing precision for analysis of munitions



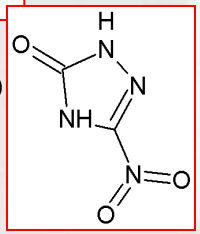
Assessing the Fate and Transport of IMX Formulations in Soils

- **Funding source**: ERDC Environmental Quality Basic Research Program 6.1 (TDs: Savoie, Ferguson)
- **Duration**: FY12 - 14
- **PIs**: Seiter, Jung, Russell, Chappell
- **Objective**: Determine the biogeochemical factors impacting the environmental fate and transport of the IMX-101 and IMX-104 formulations in soil
- **Results**: pending
- **BLUF**: provide predictive information on the mobility of IMs based on site specific soil physicochemical properties. Information generated will aid in the management of the use and potential remediation efforts at firing ranges.



Small scale soil column studies (left)

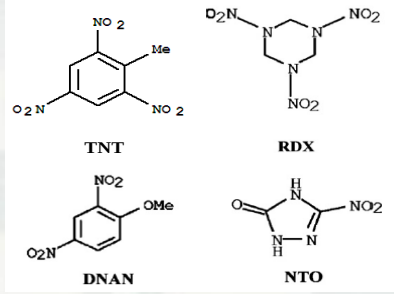
Firing of M795 155mm projectiles (below)



Extreme Sensitivity of Amphibian Development and Survival to MC Exposure: A Comparison of MC and IM Toxicity and the Mechanisms Impacting Development.

- **Funding source**: ERDC Environmental Quality Basic Research Program 6.1 (TDs: Savoie, Ferguson)
- **Duration**: FY12 - 14
- **PIs**: Dr. Kurt Gust
- **Objective**: Characterize traditional and insensitive munitions (IMs) impacts on amphibian larvae to manage a candidate for T&E status that inhabit military installations across the Southeastern US.
- **BLUF**: Research will employ molecular mechanisms of Action to robustly test if IMs are safe alternatives to MCs regarding environmental risk on T&E species

Insensitive Munitions can Protect Soldiers. Can they also protect the Environment?



Summary

- IM advantages
- Sustainable materials
  - Advance Army mission while maintaining environmental compliance
- Relative IM toxicity
  - DNAN less toxic than other munitions
- Advantage of proactive environmental information
  - Anticipation worse than reality
- ERDC goal: conduct basic and applied research to address IM environmental knowledge gaps

Contact information

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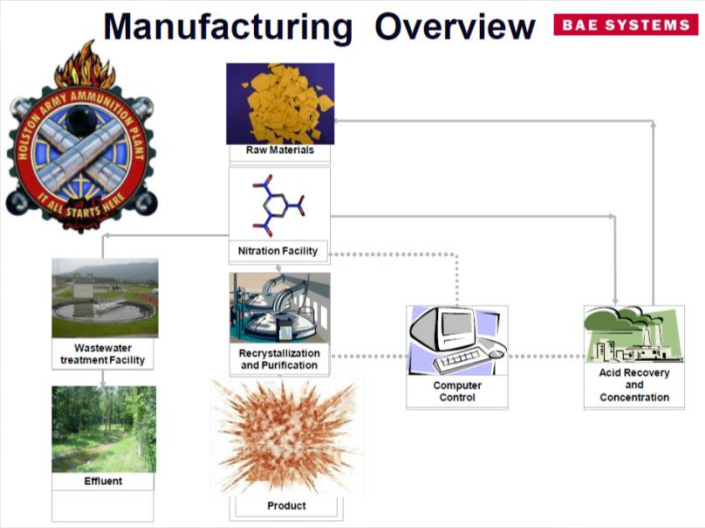
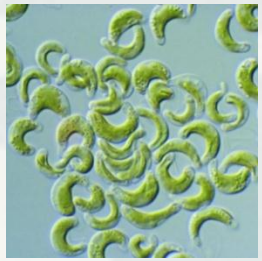
Manufacturing

- Holston Army Ammunition Plant
  - IMs incorporated into permit – no specific limits
  - Potential to treat via Fenton's reaction (Dr. David Gent)
- Iowa Army Ammunition Plant



WET testing

- WET = whole effluent toxicity testing (bioassays)
  - Vertebrate, invertebrate and plant recommended (40 CFR Part 122.44(d)(1)(ii))
  - RWC = receiving water concentration
  - 100% effluent, (RWC+100)/2, RWC, RWC/2, RWC/4
- Aquatic
  - Acute
    - 48 to 96-h *Daphnia magna/pulex*
    - 48 to 96-h *Ceriodaphnia dubia*
    - 48 to 96-h *Pimephales promelas*
    - 48 to 96-h *Oncorhynchus mykiss*
  - Chronic
    - 7-d *Ceriodaphnia dubia*
    - 7-d *Pimephales promelas*
    - 4-d *Selanastrum capricorntum*



Development of Environmental Health Criteria for Insensitive Munitions

- **Funding source**: Strategic Environmental Research and Development Program (SERDP)
- **Duration**: FY12 - 14
- **PIs**: Dr. Mark Johnson
- **Objective**: Generate the toxicological data that regulators require for NPDES permitting
- **Results**: **PLACEHOLDER**
- **BLUF**: **PLACEHOLDER**